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Equation of state of dense Hydrogen and the plasma phase transition; A microscopic calculational model for complex fluids

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Abstract

We discuss problems related to the electronic and ionic structure of fluid Hydrogen, for equation of state calculations in the domain where a "plasma phase transition" (PPT) may occur. It is argued that the ionization of an electron bound to a particular nucleus proceeds through a progressive delocalization involving "hopping" electron states (i.e. cluster states). A description of the plasma containing pseudoatoms, pseudomolecules and free electrons is proposed. The PPT, if it exists, might be a mobility edge transition across a percolation threshold. It is shown how the effect of electron density, field-particle distributions and temperature on the binding energy of these pseudoatoms and pseudomolecules, can be included. Finally the abundances of these objects is determined by a minimization which allows the self-consistent optimization of ionic as well as electronic parameters contributing to the total free energy.

On discute les problèmes associés à la structure electronique et ionique de l'Hydrogène en phase fluide, en vue de calculs d'équation d'état dans le domaine d'une éventuelle transition de phase vers l'état de plasma (TPP). L'argument essentiel est que l'ionisation d'un électron lié attaché à un atome se produit par une délocalisation progressive mettant en jeu des "états de grappe" (cluster states). La TPP pourrait être une transition de la mobilité se produisant au seuil de percolation. On propose une description du plasma où "pseudoatomes", "pseudomolécules" et électrons libres coexistent. On

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montre comment la densité électronique, le profil des particules de champ et la température peuvent être pris en compte dans l'énergie de liaison de ces pseudoparticules. Finalement, l'abondance de celles-ci doit être determinée par une minimisation qui assure l'optimisation simultanée des paramètres ioniques et électroniques, de manière autocohérente.

12.1 Introduction

Density functional theory (DFT) is a very effective many-body technique (Hohenberg and Kohn 1964, Kohn and Sham 1965) for calculating the electronic and structural properties of atoms, solids, liquids and plasmas (Lindqvist and March 1983, Gross and Dreizler 1994). Finite temperature DFT (Mermin, 1965) proceeds via the Mermin-Kohn-Sham variational principle which asserts that the thermodynamic potential (TP) is a unique functional of the one-particle densities of the system and that the TP is a minimum for the true (physical) densities. Thus a DFT calculation should provide all the ingredients needed for a microscopic calculation of the equation of state (EOS) of a given system. In an elemental plasma, e.g., an Al-plasma at high temperatures, one of the complications is the existence of several ionization states, e.g., $Al^{z_i^+}$, with $z_i = 0, 1, 2, ..., Z$. Thus there are $Z + 1$ ionic species and electrons, i.e., a $Z + 2$ component system, with concentrations x_i and a mean ionic-charge $Z^* = < x_i Z_i >$. In the "average neutral-pseudoatom" approach the $Z + 1$ ionic species are replaced by one ionic species with "average" charge Z^* and the EOS is determined in that simplified model. The name "neutral pseudo-atom" (NPA) refers to the neutral object consisting of an ion in a suitable profile (e.g., a Wigner-Seitz cavity) plus its cloud of bound and free electrons that form a neutral object (a more rigorous definition is given in terms of a sum rule on the phase shifts). The bound and free-electron distribution etc., at the NPA are determined by the self-consistent solution of Kohn-Sham equations for the electrons and ions in the plasma (Dharma-wardana and Perrot, 1982, and 1987). In the average-NPA approach the individual species concentrations x_i are not evaluated and hence Z^* is fixed by other considerations, e.g., as in the studies of the EOS of dense Al (Perrot 1990) and Be (Perrot 1993). Recently we have implemented a DFT calculation of the EOS of the $Z + 2$ component mixture without appealing to the so called "chemical pictures", hard-sphere models etc. In this approach we construct $Z + 1$ different neutral pseudoatoms (each self-consistently determined for the given plasma conditions) and use their interactions with one another and with electrons, instead of a single average-NPA which interacts with the electrons.

The above discussion of metallic plasmas takes on a new dimension of difficulty at lower densities and temperatures when molecule formation becomes important. Alkali metal vapors and Hydrogen plasmas have some similarities in this regard. Thus, a hydrogen plasma at 0.25 Mbar and 1eV could contain H_2, H, H^+, e^- and possibly H^-, H_2^+, and small amounts of other clusters. As the density is increased the identity of these" chemical" objects becomes "blurred". Thus an excited H_2 molecule having a "bond length" R begins to resemble two unbound hydrogen atoms separated by a distance R. In effect, if mean distances become comparable to bond lengths the simple "chemical" picture breaks down. Even if chemical species like H_2, H^+, etc., could be identified, their electronic energy levels, vibrational spectra etc., have to be calculated self-consistently, including the interactions with the medium, i.e., the field-particles (FP) that surround a given "molecule-like" entity.

Progress in this type of problem is easier for vapors of simple metals for which pseudopotential theory is applicable. The problem is more difficult for protons where the full non-linear consequences of a point-charge (with no moderation effect arising from a finite core size) have to be taken into account and no meaningful construction of pseudopotentials is possible. Thus in our study of ionized hydrogen plasmas (Dharma-wardana and Perrot 1982) we retained electron- and ion- coordinates at every stage of the calculation, and avoided pseudopotentials or linear response.

The objective of this paper is to examine a tractable microscopic approach to EOS of hydrogen fluid in the proposed plasma phase transition (PPT) regime (Saumon and Chabrier 1992) where molecular species exist. It is useful to examine not just the thermodynamics, but also the dynamical process of ionization. Such a study sharpens our concepts about the PTT and leads the way for a future numerical study of this difficult regime of hydrogen fluids.

12.2 The mechanism of ionization

Wigner and Huntington (1935) noted the similarities between hydrogen and the alkalis and sowed the seeds leading to the concept of a plasma phase transition (Stevenson and Salpeter 1977, Ebeling and Richert 1985). The most elaborate study of the PPT is due to Saumon and Chabrier (1992). They considered a hydrogen fluid containing the four species H_2, H, H^+, e^- and found that a fluid phase which was predominantly H_2, with very low ionization ($x_{H+} < 0.5\%$) and low monatomic H concentration undergoes a first order phase transition to a significantly ionized ($x_{H+} \approx 25\%$)

fluid phase, still containing H_2, H, H^+, e^-, at $T_c = 1.3$ eV and $P_c = 0.614$ Mbar corresponding to a critical density of 0.347 g/cc. Since a sharp increase in ionization is proposed, it is important to understand the process of ionization.

Ionization of a single atom in the vacuum is the promotion of an electron from some bound state $\nu = n, l, m$ of energy $-|\epsilon_\nu|$ to a continuum state k, l, m with energy $k^2/2$ (here we use atomic units: $\hbar = 1$, $|e| = 1$, $m_e = 1$). In Hummer and Mihalas (1988), and in Mihalas, Hummer and Däppen (MHD, 1988) the ionization process is modeled by assuming that the field particles (FP) create a microfield which Stark ionizes the atom. However, if an effectively spherically symmetric potential were applied to the atom (this could happen from a cubic packing of a coordination shell of FP around the atom) the microfield is zero but a very large destabilization of the atomic bound state could arise. Thus the MHD model is incorrect from the outset. The MHD-estimates of the "critical fields" for ionization of atoms do not contain effects of possibly large potential fluctuations and electron-exchange effects which nevertheless have small microfields (note that the fields are vectors, while the potentials are scalars). Ionization from metal clusters, and the workfunction of metal surfaces are known to be strongly determined by the exchange energy of the ionizing electron, i.e., a quantum effect unrelated to the Stark effect. The discussion given below suggests that the ionization process involves cluster states of the FP in a fundamental way.

Consider an atom in a plasma. For simplicity, let the inner shells of the atom be full and let the last occupied electron (in the ground state) be ns where n is a principle quantum number. The "radius" of the atom is about n^2 atomic units (a.u.). Consider a dilute plasma of atom density ρ_a where the mean separation $r_{ws} = (3\rho_a/4\pi)^{1/3}$ is large, say $100\,n^2$ a.u. An ionizing electron acquires energy from the FP via thermal and random fluctuations of the particle distribution. Most collisions are long-range, weak, multiple collisions which slowly raise the electron to higher energy levels. When the electron reaches the excited state with $n_f = 10n$ the electron is still in a bound state but the "size" of the atom is comparable to the inter-atomic distance r_{ws}. From then on the electron gains energy by hoping to orbitals which span several atomic centers (i.e, clusters) prior to ionization. That is, the atomic electron becomes a "hopping electron" before it passes into the continuum to become a fully delocalized ("free") electron.

Thus the ionization process involves three types of electrons, viz., bound, hopping and free electrons. The discussions in terms of only bound electrons and free electrons apply only in situations where hopping electron concentrations are negligible. Unfortunately, hopping electrons are important except

in fully ordered solids at zero temperature, or in very hot strongly ionized plasmas. The theory of hopping electrons, and the relationship of the ionization process to the concept of the "mobility edge" transition (see Davis and Mott 1975) present in disordered materials apply to plasma situations as well (Dharma-wardana and Perrot 1992). The same ideas are relevant for an understanding of the PPT.

The cluster ionization picture can be restated as a local-band theory of disordered materials. Consider a Hydrogen fluid in the weakly ionized pre-PPT phase of Saumon and Chabrier (to be denoted the prephase, while the phase with a higher ionization will be called the postphase). The prephase is mostly H_2 molecules. If we sit on an H_2 molecule (the origin), then there is local order as defined by the range R_c beyond which particle correlations die-off and the pair function $g(r)$ becomes essentially unity. This is effectively the "cluster" to consider. We could either think of cluster states or of a local bandstructure in the region $r < R_c$ around the molecule at the center. Electron hopping will be determined by a matrix element $T(r_{ij})$ linking atomic centers i and j, and determines the local bandwidth. In H_2 this band is fully occupied at T=0K and hopping occurs by transferring to the unoccupied conduction band, or via an upper "Hubbard band" if that is energetically more favorable (the upper Hubbard band of H_2 is approximately the valence band of H_2^-). However, the situation becomes radically different if even a small amount of H_2^+, H^+, etc., and electrons are also present, as in the prephase. Then we have a small number of holes in the H_2 local-valence band, a few electrons in the local-conduction band, as well as "impurity gap states" of H_2^-, H_2^+, H^+, H and H^- structures (the H and H^- bandstructures are essentially like the lower and upper Hubbard bands of H). The gap states provide a degree of hopping conductivity via overlapping localized states, but the mean free path of the hopping electron remains smaller than the cluster size R_c. However, when the percolation threshold (e.g. Stauffer 1979) is reached the hopping paths "percolate" through the whole volume and provide at least one electronic state which carries the electron out of the cluster. This is the onset of the so-called mobility edge and amounts to a phase transition in the sense that localized carriers have now become delocalized. The idea of the mobility edge was first presented by Mott and further developed by many authors (see Davis and Mott 1975). It is very likely that if the proposed PPT exists, then it is essentially a transition across the mobility edge, and its existence depends on the sharpness of the mobility edge. Note that crossing the mobility edge to reach the more conductive postphase does not require that the carriers have reached the conduction band - they have merely crossed into the per-

colating impurity states in the local band gap. The postphase need not to be a fully ionized phase, as has been assumed by some authors.

The cluster picture of ionization involves a gradual delocalization of a bound electron on a given atomic site to occupy increasingly larger-sized bound states defined on a local transient cluster (hopping states) and finally in the whole plasma (full ionization). This picture is more convenient than the local-band picture with gap states. However, the two models complement and clarify the nature of the ionization process and the PPT.

In an earlier study (1982) we considered a hydrogen plasma where each proton supported only one bound state. A significant feature of the bound 1s-state reported in that study was that its average radius was larger than the mean proton-proton separation i.e., a hopping state. The bound state was calculated with the proton interacting with an "average" cluster of field ions (FI) and electrons around a proton. The FI-cluster is modeled by the ion distribution $\rho g(r)$, where ρ is the average (bulk) nuclear density. Although such an "average cluster" is incorrect at short time scales, it is valid for thermodynamics which depend only on space and time averaged quantities. To treat the molecular species present in the prephase and the postphase, a multi-center model is needed and will be taken up next.

12.3 Construction of pseudoatoms and pseudomolecules

In the so called "chemical" picture for EOS calculations one assumes (by "chemical intuition") that certain well defined chemical species, e.g., H_2, H, etc., exist in a given fluid and that their "internal" electronic coordinates do not appear in the discussion. Instead, energy spectra and weights of isolated molecules appear in "internal" partition functions. The internal partition functions of isolated atoms or molecules contain divergencies which are removed by various prescriptions. In a more fundamental analysis (sometimes called the "physical picture") electrons and nuclei interact via the Coulomb interaction, and the interplay between the electron coordinates and the nuclear coordinates is retained right up to the final stage of free energy minimization which determines the mixture composition, particle distributions and the thermodynamics. Even in the physical picture we can talk of molecular species noting that these are "pseudomolecules" (PM) which are "coupled to each other" since the internal structure of a PM depends on the environment around it, i.e., the self-consistent distribution of field particles around it. In the low density limit these PM reduce to the molecules of the chemical picture. Also, the pair-interactions of the PM will

be a function of the particle distributions in the medium which have to be generated in situ while the free-energy is minimized.

If we consider the prephase and the postphase of the PPT, then we need to construct pseudomolecules like H_2, H, H_2^+, H^+, H^-, H_2^- in the presence of the equilibrium concentration of electrons, at a given temperature and total density. Here an H^+ is really a proton carrying no bound electrons, plus a distribution of electrons, ions, and other molecular species (the field-particles), while H and H^- carry a singly or doubly occupied bound state which spills into the respective self-consistent FP-distribution (FPD). These field-ion distributions are given by the classical form of the Kohn-Sham equations, while the boundstates and field-electron distributions are given by the (quantum) Kohn-Sham equations which are coupled to the classical equations. The electron coordinates and the ion coordinates are retained through out the energy minimization. Unfortunately, this procedure is numerically too arduous since we need to self-consistently resolve a multi-center, multi-species problem as well as quantum mechanical problems for bound and continuous spectra. Hence we consider a less ambitious procedure based on using single-center DFT calculations to construct a tight-binding-type model to account for the molecular states of the pseudomolecules.

12.3.1 Tight binding model

A hydrogen atom placed in a given field-particle distribution (FPD) will have a finite set of bound states ϕ_ν , $\nu = n, l, m$ and energy ϵ_ν as well as a spectrum of scattering states $\nu = k, l, m$ with $\epsilon_\nu = k^2/2$. From our previous work (single center calculations) we know how to determine this Kohn-Sham energy spectrum of bound and free states for a given FPD. To simplify the discussion we assume that there is only one bound state, u_{1s}, but several bound states would be needed in many applications. We fit the $u_{1s}(r)$ function to the form $u(Z^*, r) = (Z^{*3}/\pi)^{1/2} exp(-Z^* r)$. This simple form where Z^* is the only fit-parameter is probably adequate for the plasma-problem. Although we are concerned with H-plasmas, we also carry out single-center calculations for the He^{++} and He^+ ions in the given FPD and determine their Kohn-Sham spectra. He^{++} and He^+ correspond to the "zero bond length" limit of two protons, or a proton and an H atom. This "united-atom" limit of the molecular species is required to correctly recover the interaction energies at smaller particle separations. Now we consider the construction of pseudomolecules.

12.3.2 H_2^+ *pseudomolecule*

The electron Kohn-Sham equation for the H_2^+ molecule in the fluid is :

$$
\left[\frac{p_e(\vec{r})^2}{2} - \frac{1}{r_A} - \frac{1}{r_B} + \frac{1}{R} - V_p\{\vec{r}, n(\vec{r}), \rho(\vec{r})\} \right.
$$
$$
\left. + V_{xc}\{\vec{r}, n(\vec{r}), \rho(\vec{r})\} \right] \psi(r, R) = E\psi(r, R) \tag{1}
$$

Here R is the internuclear separation between the protons labeled A and B; the electron coordinate $\vec{r}$ referred to the midpoint, and to the centers A and B are related by $\vec{r}_A = \vec{r} + \vec{R}/2$ and $\vec{r}_B = \vec{r} - \vec{R}/2$. Also V_p and V_{xc} are the Poisson potential and the exchange-correlation potential due to the FPD. The xc-potential is a density-functional potential which brings in the many-body effects of exchange and correlation with electrons, and correlations with ions. Their formulation has been discussed in our earlier work (e.g., see Perrot, Furutani and Dharma-wardana, 1990). An approximate construction of V_p and V_{xc} for the two-center problem is given below. Consider the isolated molecule where V_p and $V_{xc} = 0$. In the limit where R is large we have two (gerade and ungerade) solutions :

$$
\psi(r, Z^*, R)_{g,u} = [u(Z^*, r_A) \pm u(Z^*, r_B)]/2^{1/2} \ \ \text{large } R \text{ limit} \tag{2}
$$

with $Z^* = 1$ and the energy

$$
E_{g,u} = \epsilon_{1s} + R^{-1} \frac{\left[(1 + R)e^{-2R} \pm (1 - 2r^2/3)e^{-R} \right]}{[1 \pm (1 + r + R^2/3)e^{-R}]} \tag{3}
$$

However, this is a poor solution for small R. In the $R \approx 0$ limit we use a value of $Z^* = Z_0$ consistent with the solution of the He^+ problem, i.e., the "united atom" obtained from H_2^+. That is, we find $Z^*(R)$ variationally for each R for the isolated H_2^+ problem so that

$$
Z^* = Z_0 f(R) + Z_\infty \{1 - f(R)\} \tag{4}
$$

interpolates from $R = 0$ to $R = \infty$, with $Z_\infty = 1$. The minimum of $E_g(R)$ at $R = R_0$ is the binding energy with the optimal $Z^*(R_0)$. This approach provides an excellent solution to the H_2^+ problem (i.e., to the accuracy we needed for the plasma-fluid problem) since the experimental (Herzberg 1954) binding energy $E_b = E_g(R_0) - \epsilon_{1s} = -2.79$ eV and $R_0 = 2.003$ a.u.,

while this method (Bransden et al 1983) gives $E_b = -2.25$ eV and $R_0 = 2.0$ a.u. with the optimal $Z^*(R_0) = 1.23$. The vibration- and rotation- spectra can be calculated as usual from $E_b(R)$.

Now consider the pseudomolecule H_2^+ in the presence of the FP (e.g., H_2, H, H_2^+, H^+, H^-, H_2^- etc). A given FPD can be rewritten as a density $\rho(\vec{r})$ of protons and a density $n(\vec{r})$ of electrons. The $\rho(\vec{r})$ and $n(\vec{r})$ interacting with the pseudomolecule whose mid-point is at the origin of coordinates produce the potentials $V_p(\vec{r})$ and $V_{xc}(\vec{r})$. These potentials are constructed from the one-center functions $V_p(\vec{r}, H), V_p(\vec{r}, He^+)$ and $V_{xc}(\vec{r}, H), V_{xc}(\vec{r}, He^+)$ which are known from the single center calculation for H and He^+. In effect we define

$$
\begin{aligned}
V_p(\vec{r}) = {} & V_p(\vec{r}_A, He^+)F(R) \\
& + \frac{1}{2}\{V_p(\vec{r}_A, H) + V_p(\vec{r}_B, H)\}\{V_p(\vec{r}_A, H^+) + V_p(\vec{r}_B, H^+)\} \quad (5) \\
& \times \{1 - F(R)\}
\end{aligned}
$$

where the superposition takes place in the independent atom limit for very large R, while for small R we recover the united-atom limit of He^+. The interpolation function $F(R)$ could be modeled by $f(R)$ of Eq. (4) or a better form can be constructed. The same interpolation scheme can be used for constructing $V_{xc}(\vec{r})$ from the results of the one-center calculation and hence all the potentials need in the two-center Kohn-Sham equation, i.e., Eq.(1) are known. Now in variationally determining Z^* appearing in $\psi(r, Z^*)$ we do not use just Eq.(3) but include also the FP-energy contribution, i.e. $< \psi(r, Z^*)|V_p(\vec{r}) + V_{xc}(\vec{r})|\psi(\vec{r}, Z^*) >$. This will give us a new $Z^*(R, \rho, n)$ to replace Eq.(4), where the limiting forms Z_0 and Z_∞ correspond to the He^+ and H atom wavefunction-exponents from the one-center calculations with the field particles self-consistently included. A new binding energy curve $E_b(R, \rho, n)$ dependent on the FP-distributions $\rho(\vec{r})$, and $n(\vec{r})$ and a new intermolecular equilibrium distance R_0 will result from this calculation. If there are no H_2^+ molecules in the system under the assumed conditions, then there will be no stabilizing minimum and $E_b(R) > 0$. Thus the method by itself determines the pseudomolecules found in the fluid, independently of any "chemical intuition". The binding energy curve $E_b(R, \vec{r}, n)$ of H_2^+ calculated here is basically the interaction potential between an H atom and an H^+ ion separated by a distance R in the fluid, inclusive of all the fluid effects. Given $E_b(R, \vec{r}, n)$, the vibrational and rotational spectra and the "internal partition function" can be calculated as usual.

The concept of an internal partition function has a meaning only if an

"internal part" and an "external part" can be defined. Since the Kohn-Sham calculation includes the whole "correlation sphere" or cluster defined by the FPD, this issue is non-trivial. In the usual neutral-pseudoatom calculations (e.g. Perrot 1993) for simple metallic fluids, it is sufficient to use a spherical Wigner-Seitz cavity to represent the FPD at the pseudo-ion. The effect of the cavity is corrected for using linear response theory applied to the electron gas. In more complicated pseudomolecular systems the simplifications available for "simple metallic" fluids are not present. However, the effect of the FPD can be allowed for and factored out consistently by using a response function constructed from the Kohn-Sham basis of the pseudomolecule, instead of the response function constructed with plane wave states. Then the numerical work is more demanding. Simplified approaches using Wigner-Seitz volumes for each pseudomolecule and projecting out the contributions from neighboring cells according to some physical scheme etc may also be used. Since the electronic spectra contain only finite numbers of bound states, there are no spurious degeneracies appearing in the partition function summation.

The electron density $n(\vec{r})$ will be adjusted to self-consistence but the 2-center FPD is not reevaluated except in the singe-center step. That is, the electron density results, bond lengths etc., of the two-center step are inputs to recalculate the self-consistent FPD of the one-center step. This approach is valid to second order in the density corrections, and has given good results in other problems (e.g., see Harris 1987).

12.3.3 H_2 pseudomolecule

Here again we begin with a simple one-parameter model of the isolated H_2 molecule and re-optimize this parameter as a function of the field-particle potentials $V_p(\vec{r})$ and $V_{xc}(\vec{r})$. For constructing the H_2 pseudomolecule we use as our tight-binding basis a generalization of the solutions $\psi(r, Z^*, R)$ of the H_2^+ system. The simplest symmetric form for the spatial part of the H_2 wavefunction (singlet spin state) is :

$$\Phi(r_1, r_2) = \psi(r_1, Z^*, R)_g \psi(r_1, Z^*, R)_g$$

This can be rewritten in terms of the atomic 1s-functions as

$$\Phi(r_1, r_2) = \Phi_{cov}(r_1, r_2) + \Phi_{ion}(r_1, r_2) \tag{6}$$

where

$$\Phi_{cov}(r_1, r_2) = [u_{1s}(r_{A1})u_{1s}(r_{B2}) + u_{1s}(r_{A2})u_{1s}(r_{B1})]$$

$$\Phi_{ion}(r_1, r_2) = [u_{1s}(r_{A1})u_{1s}(r_{A2}) + u_{1s}(r_{B2})u_{1s}(r_{B1})]$$

Instead of Eq.(6) we use the trial form

$$\Phi(r_1, r_2, Z^*, \lambda) = (1 - \lambda)\Phi_{cov}(r_1, r_2) + (1 + \lambda)\Phi_{ion}(r_1, r_2) \qquad (7)$$

where λ is the new variational parameter. That is, $Z^*(R)$ is the value determined to be optimal for the H_2^+ problem and λ is specific to the H_2 problem. We may also optimize both Z^* and λ, with improved results. Using this approach for isolated H_2 a binding energy $E_b(R_0) = -4.00$ eV and an equilibrium bond distance $R_0 = 1.5$ a.u, are obtained (cf. experimental values (Herzberg 1954) $E_b = -4.7$ eV, $R_0 = 1.4$ a.u.).

In the pseudo-H_2 system inclusive of FPD we have to construct the two-center potentials $V_p(\vec{r})$ and $V_{xc}(\vec{r})$. We interpolate between the infinite-R limit where $V_p(\vec{r})$ is a superposition of two single-center $V_p(\vec{r})$ H-atom potentials calculated using the single-center DFT equations, and the $R = 0$ united-atom limit which is the He-atom. The interpolation function $F(R)$ is similar to that of Eq.(5), and constructed using results of trial calculations. Once the potentials $V_p(\vec{r})$ and $V_{xc}(\vec{r})$, and the limiting $Z^*(R, \vec{r}, n)$ values for $R = 0$ and $R = \infty$, are prepared from the one-center calculations for H and He pseudoatoms, λ is now minimized (for each R) including the FP-term, i.e. $< \phi(r_1, r_2, Z^*, \lambda)|V_p(\vec{r}) + V_{xc}(\vec{r})|\phi(r_1, r_2, Z^*, \lambda) >$. The resulting binding energy curve $E_b(R, n, \rho)$ of pseudo-H_2 in the fluid can be used to obtain the vibrational and rotational spectra and the "internal partition function" inclusive of the effects of the fluid environment. If the binding energy function $E_b(R, n, \rho)$ has no minimum at some R_0 then the fluid does not support the existence of H_2 molecules.

12.3.4 *Other pseudo-molecules and clusters*

These methods can be applied to almost any simple hydrogenic cluster. We begin with a simple tight-binding model for the cluster in isolation and then include the FPD via the optimization of a relevant parameter in the Kohn-Sham functions used in the tight-binding model. The method also yields interaction potentials between pseudomolecules without resorting to perturbation theory. Thus we may consider the interaction between

an H_2-pseudomolecule with an H^+ ion in the fluid. The H^+ ion has a FPD around it. The construction of the potential around the pseudo-H_2 molecule was already discussed. Hence if we have to consider the interaction potential between a pseudo-H_2 molecule and a pseudo-H^+ ion, we use the $\Phi(r_1, r_2, Z^*, \lambda)$ solutions of the previous problem and taking a linear combination involving Φ_{AB}, Φ_{BC}, and Φ_{CA} where A, B, and C are the three nuclei of the H_2 and H^+ interacting system. This includes the binding due to electrons hopping among the three nuclei and goes beyond the usual polarization potential models for the H_2-H^+ interaction. A three-body interaction-potential (which is what the H_2-H^+ system is) can be reduced to a 2-body potential either by imposing an equilibrium bond distance R_0 to one of the three inter-nuclear separations (valid if the other two distances are $>> R_0$), or by averaging with pair-distributions functions, as in Aers and Dharma-wardana (1984).

The method proposed here is free of hard-sphere models, cutoffs in the partition function etc. It provides a microscopic approach which is capable of (i) determining the stability of a given pseudo-molecular cluster in the fluid and hence deciding whether we need to include it in the thermodynamics, (ii) providing environment-dependent binding energy functions and interaction energy functions, (iii) providing the "internal partition function" of each species taking account of interactions with the plasma, (iv) obtaining triplet and singlet spin states, $\sum$, Π momentum states etc., and their correct thermal averages.

12.4 Minimization of the free energy function

It is convenient to rewrite the free-energy minimization step outside the multispecies density functional calculation which involves the self-consistent resolution of a set of coupled Kohn-Sham equations for each species, as well as electron spectra for each species. Then the proposed procedure is as follows:

(i) We prepare a trial "mixture" of species like H_2, H, H_2^+, H^+, H^-, H_2^-, e^- at mean nuclear density ρ_n and compositions x_i. The electron density is constrained by charge neutrality.

(ii) Single-center DFT calculations are done for the united-atom and single atom limits, viz., for He, He^+, H^+, H, H^-, and He^-. The FPD can be simplified if desired, by replacing the FP-molecules by simpler distributions. Thus an H_2 molecule is replaced by a distribution of electrons centered at the mid-point of the H_2-bond and calculated from $|\Phi(r_1, r_2, Z^*, \lambda)|^2$. The electrons contribute $n(r)_{H_2}$ to the total electron distribution $n(r)$. We also

include the two nuclei which contribute $\rho(\vec{r})_{H_2}$ to the proton distribution $\rho(\vec{r})$. These contributions $n(\vec{r})_{H_2}$, $\rho(\vec{r})_{H_2}$ have no effect on the Poisson and xc-potentials (in the local density approximation) unless $n(\vec{r})_{H_2}$ has some overlap with the pseudomolecule at the origin whose detailed structure is being calculated. The existence of any overlap leads to hopping electronic states which cause modifications in the spectrum of the central particle.

(iii) The output from the single center calculations will be electron distributions and FP-distributions.

(iv) These are now fed into the multi-center calculations for pseudomolecules. We do not directly solve multicenter Kohn-Sham equations, but use the tight-binding approach where one or two carefully chosen parameters determining the bound state wavefunctions are optimized. The FPD and the continuous electron spectrum are interpolated from the single- and united-atom limits as discussed before, in the spirit of the Harris functionals.

(v) The new electron distributions are introduced into step number (ii) above.

(vi) Step (iv) is repeated and interaction potentials, binding energy curves and the internal partition functions are calculated.

(vii) A more refined evaluation of the FPD, using the interaction potentials obtained at this stage may be carried out using MD or integrals equations (N.B. The DFT equation for classical particles are formulated as an effective HNC equation, coupled to the electronic Kohn-Sham equation).

(viii) A total free energy minimization is carried out to obtain the mixture composition x_i.

(ix) These new x_i are fed into step (ii) and the procedure is repeated until self-consistency is attained.

(x) At this stage the mixture composition, particle distribution functions, interaction potentials etc.. are completely converged. The equation of state, electrical conductivity (Perrot and Dharma-wardana 1987), thermal conductivity and other properties which could serve as a "diagnostic" of a phase transition can be calculated at this stage.

Thus the free-energy minimization step (i.e., step viii) is carried out within the large iterative loop (steps ii to viii) where the adjustment of the internal electronic coordinate is carried out in consort with the evaluation of FPD and the structure and spectra of the pseudomolecules. This is exactly the "physical picture" of a microscopic theory.

In this discussion we have not addressed a number of issues. We assume that the protons can be treated as classical particles. Also, when an ion is immersed self-consistently in a fluid containing continuum ("free") electrons, the continuum density of states becomes modified. The effec-

tive masses m^* of the electrons near each pseudomolecule change from the usual value of $m^*/m_e = 1$, and the existence of finite sized bound cores on each ion also affect the compressibility of the electron gas. All these subtle effects contribute to the electron partition function and have to be consistently treated. These issues are basically simpler than the pseudomolecular problems discussed here, and have been adequately treated elsewhere by us, in a recent (unpublished) study of Al-plasmas.

12.5 Conclusion

We have presented a tractable microscopic approach to the study of complex fluids containing neutral and charged molecular species and electrons. The intuitive "chemical picture" based on data relevant to isolated molecules, hard spheres etc., is no longer needed. The model is able to take into account the electronic interactions between molecular species and the fluid environment. This allows room for three types of electrons, viz., (i) electrons fully localized on the molecular species, (ii) electrons which hop between the molecular species and the neighboring molecules in the fluid , and (iii) fully delocalized (i.e. "free") electrons. It is suggested that the prephase of the PPT is a system with a high population of hopping electrons, while the postphase is rich in delocalized electrons. The PPT is really a transition across the "mobility edge" and its physical reality depends on the sharpness of the associated percolation threshold.

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